

portions of the nebula. 30 Dorado shows the nitrogen line with facility; the second line certainly, but not in all positions, and always with difficulty; the hydrogen line is suspected only. I can see no trace of a continuous spectrum.

$\eta$  Argo has been observed on only one unfavourable morning; the nitrogen line was seen over a considerable space; of the presence or absence of others, or of a continuous spectrum, I am unable to speak with certainty.

With respect to future operations, it is intended that at first the routine work shall consist of a detailed delineation of the objects figured by Sir John Herschel, or any others which may prove interesting: this will take some time; for even without the impediment of cloudy weather, the delineation, with any degree of satisfactory correctness, of a moderately large nebula requires a considerable amount of work and careful and frequent scrutiny. It is hoped, however, that this work will by practice be found less painfully difficult than it is at present.

The spectroscope will be used as much as possible, the moon photographed, and attempts made to photograph the nebulae, when a photographic apparatus has been procured, and staging, photographic room, &c. added to the building. It is, moreover, hoped that before long a refractor, of some nine inches aperture, may be procured, to be mounted with the reflector, or, preferably, as a separate instrument.

This telescope, besides being of much general use, will find much and valuable employment in determining micrometrically the chief points in the nebulae under examination with the reflector, with more expedition and accuracy than at present; for spectroscopic work this telescope would be a valuable adjunct, especially if it be constructed of such comparatively short focal length as seems now to be practicable.

The great interest which the Royal Society has taken in everything connected with the Melbourne reflector is my sole apology for sending thus early such a meagre account.

*February 24, 1870.*

Lieut.-General Sir EDWARD SABINE, K.C.B., President, in the Chair.

The following communications were read:—

I. "Note on certain *Lichens*." By JOHN STENHOUSE, LL.D., F.R.S., &c. Received January 10, 1870.

Through the kindness of W. Carruthers, Esq., of the Botanical Department of the British Museum, I obtained a considerable quantity of lichens from the neighbourhood of Moffat in Scotland. These were *Cladonia rangiferina*, and a mixture of *Usnea barbata* and *Evernia prunastri*,

the latter of which were carefully separated by picking—a somewhat tedious operation, as they were much interlaced.

*Usnea barbata.*

In order to extract the usnic acid from this lichen, it was macerated for about thirty minutes with a dilute solution of sodic carbonate, squeezed, again treated once or twice in a similar manner, and the turbid solution precipitated by a slight excess of hydrochloric acid. The crude dark-green acid thus obtained was mixed with milk of lime and a considerable quantity of warm water (40° C.), filtered, and the clear lemon-coloured solution of usnate of calcium acidulated with hydrochloric acid. The acid was thus precipitated in pale yellow flocks, which were collected.

The reason that I adopted this modification of the process I formerly proposed\* is, that although usnic acid readily dissolves in milk of lime when it has been extracted, yet in order to exhaust this and other compact lichens, it requires to be treated a great many times if lime be employed, whilst two or three are sufficient with carbonate of sodium.

The partially purified usnic acid obtained in the manner above described was easily rendered quite pure by taking advantage of the peculiar property which this acid possesses of forming an insoluble calcium salt when boiled with lime. The crude yellow acid was placed in a flask with a quantity of water and an excess of slaked lime, and the mixture boiled for twenty minutes or half an hour. The insoluble calcium usnate was collected, well washed with hot water, and the lime then removed by boiling it with a slight excess of hydrochloric acid. The tolerably pure usnic acid was then collected, and well washed with boiling water. It was advisable to continue the digestion with hydrochloric acid for half an hour, as it rendered the acid more compact and easy to collect. By this alternate treatment with lime and acid, a large quantity of some dark-coloured impurity was removed. This forms the best process for recovering usnic acid in a state of tolerable purity from residues.

It was found, however, to be better, when considerable quantities of usnic acid were to be prepared, to boil the pale yellow usnic acid paste, as obtained by precipitation from the lime solution, with a small quantity of water, to which strong caustic soda solution was gradually added, sufficient to dissolve nearly the whole of the usnic acid. It was then set aside to crystallize, and when cold the very dark coloured supernatant mother liquor decanted, and the crystals of sodic usnate washed once or twice by decantation, with a small quantity of cold water. It was then redissolved and recrystallized once or twice in the same manner.

The nearly pure sodic usnate was now dissolved in a considerable quantity of hot spirit, filtered, and the boiling solution strongly acidulated with acetic acid. The usnic acid then separated in fine needles, which when cold were collected, well washed with cold spirit (in which they are almost

\* Ann. der Chem. und Pharm. vol. lxxviii. p. 98.

insoluble), and recrystallized from boiling spirit to render them quite pure.

When the quantity of acid operated on was but small, the best process was to dissolve it, by means of caustic soda solution, in a large quantity of boiling spirit, filter from the insoluble impurities, and strongly acidulate with acetic acid. The nearly pure usnic acid, which crystallizes out in large needles when the solution cools, was collected, washed, and recrystallized two or three times from spirit.

I. .130 grm. usnic acid gave .298 grm. carbonic anhydride and .060 grm. water.

II. .245 grm. usnic acid gave .564 grm. carbonic anhydride and .188 grm. water.

			I.	II.	Hesse.
C <sub>18</sub>	=	216	=	62.43	62.53
H <sub>18</sub>	=	18	=	5.20	62.79
O <sub>7</sub>	=	112	=	32.37	62.80
		<hr/>		<hr/>	5.00
		346		100.00	

I. was purified by boiling with lime, and II. by repeated crystallization of the crude acid from spirit.

In the analyses published by W. Knop, Rochleder, and Heldt, and also by myself in 1848, the carbon is about .75 per cent. higher than the above, and the formula deduced from it was C<sub>19</sub>H<sub>16</sub>O<sub>7</sub>. Hesse\* from his analyses proposed the formula C<sub>18</sub>H<sub>18</sub>O<sub>7</sub>, which I have adopted.

#### *Usnate of Sodium.*

This was best prepared by adding one part pure usnic acid to twenty of boiling water, and then sufficient caustic soda solution to dissolve nearly the whole of the acid, filtering, and setting aside to crystallize.

After one recrystallization it was subjected to analysis.

I. .598 grm. usnate of sodium gave .114 grm. sulphate of sodium.

II. .864 grm. usnate of sodium gave .168 grm. sulphate of sodium.

			I.	II.	Mean.
C <sub>18</sub>	=	216	=	58.70	
H <sub>17</sub>	=	17	=	4.61	
Na	=	23	=	6.25	6.18
O <sub>7</sub>	=	112	=	30.44	6.30
		<hr/>		<hr/>	6.24
		368		100.00	

This salt crystallizes in pale yellow silky needles, is not very soluble in cold water, but more so in spirit. It is readily decomposed by carbonic anhydride; so much so, that when pure sodium usnate is exposed for some time to the atmosphere, it absorbs carbonic acid, and is no longer completely soluble in water. By passing a current of carbonic anhydride through its aqueous solution, the usnic acid is entirely precipitated.

\* Ann. der Chem. und Pharm. vol. cxvii, p. 345.

*Calcium Usnate.*

When pure usnic acid was moistened with spirit, and then rubbed up in a mortar with milk of lime, it combined and formed a deep yellow paste, which, on the addition of more water and filtration, yielded a lemon-coloured solution, containing calcium usnate, and hydrate. When this solution was heated it became turbid, and after boiling some time, the whole of the usnic acid was deposited as an insoluble calcium compound, in the form of small deep yellow rhomboidal crystals. Although I made several analyses of this compound, prepared at different times, I was unable to obtain it of a constant composition, probably owing to its being mixed with variable quantities of calcium carbonate and hydrate.

The formation of this insoluble calcium salt is very characteristic of usnic acid, and is an excellent test of its presence. As with the sodium salt, carbonic anhydride entirely decomposes the calcium compound. Usnic acid appears, therefore, to be a very feeble acid.

An attempt was made to prepare *ethylic usnate* by treating usnate of silver with ethylic iodide, but without success. When usnic acid was treated with bromine it was completely decomposed, and converted into an orange-coloured uncrystallizable resin.

*Evernia prunastri—Evernic Acid.*

The evernic and usnic acids that this lichen contains were extracted by the lime process, which consists in macerating the lichen two or three times successively with milk of lime for about half an hour each time. The solution of the mixed acids was then filtered, precipitated by a slight excess of hydrochloric acid, and the precipitate collected and dried. In order to extract the evernic acid from the mixture, it was agitated for about five minutes with four parts boiling alcohol and filtered. The acids remaining undissolved were treated two or three times with the same quantity of boiling alcohol, and the dissolved evernic acid precipitated by the addition of an equal bulk of water. By this means the evernic acid, being readily soluble in boiling alcohol, was in a great measure separated from the usnic acid, which dissolves with difficulty in that menstruum unless digested with it for a considerable time. The crude evernic acid thus obtained amounted to about one-third of the mixed acids, and was purified by repeated crystallization from strong spirit, taking care not to digest it for any length of time. The process is much facilitated by completely removing the mother liquors by Bunsen's vacuum filter.

Pure evernic acid, as has been already described by myself\* and Hesse†, consists of aggregations of minute needles, melting at 164° C. It is a feeble acid, and does not decompose solutions of bicarbonate of sodium in the cold; as, however, the adhering colouring-matter is somewhat soluble in that menstruum, it may be employed to free the crude acid to a great

\* Ann. der Chem. und Pharm. vol. lxxviii. p. 84.

† Ibid. vol. cxvii. p. 298.

extent from that impurity. The solution of calcium evernate is decomposed by a long-continued current of carbonic anhydride, which precipitates calcic carbonate and unaltered evernic acid.

On theoretical grounds it has been stated\* that, by the action of potassic or baric hydrate, evernic acid should be resolved into orsellinic and evernic acids. This prediction, however, is incorrect, as I find, as formerly stated†, that evernic acid is the only fixed product.

*Tetrabrom-evernic Acid.*

Perfectly dry and finely powdered evernic acid was treated in the cold with a slight excess of dry bromine, large quantities of hydrobromic acid were given off, and a brominated compound produced. In order to prevent any portion of the acid escaping bromination, the product was finely powdered and again treated with bromine. After standing some time to allow the excess of bromine to volatilize, the finely powdered compound was well washed with bisulphide of carbon, to remove the last traces of bromine, and a small quantity of a resinous body which is produced at the same time. Two or three crystallizations from boiling spirit render it quite pure. When subjected to analysis, it gave the following results:—

I. .312 grm. acid gave .362 grm. carbonic anhydride and .067 grm. water.

II. .321 grm. acid gave .373 grm. bromide of silver.

			I.	II.
$C_{17}$	=	204	=	31.48
$H_{13}$	=	12	=	1.86
$Br_4$	=	320	=	49.48
$O_7$	=	112	=	17.28
		<hr/>		
		648		100.00

This analysis agrees very well with the formula  $C_{17}H_{12}Br_4O_7$ , four equivalents of hydrogen in evernic acid being replaced by bromine.

Tetrabrom-evernic acid is rather soluble in hot alcohol, from which it crystallizes on standing some time in small colourless prisms. It is insoluble in water and bisulphide of carbon, slightly soluble in hot benzol, and readily in ether, which when quickly evaporated leaves it as a transparent colourless resin; it melts at  $161^\circ C$ . The acid is very soluble in alkaline solutions, which on evaporation dry up to a gummy mass. When heated with concentrated sulphuric acid it decomposes.

*Usnic Acid from Evernia prunastri.*

The usnic acid left undissolved in the preparation of evernic acid usually retained traces of that acid even after repeated treatment with alcohol; but this was entirely removed by boiling with lime, as described in the first part of this paper. This decomposed and removed the evernic acid and other impurities, leaving the usnic acid in the form of an insoluble calcium

\* Watts's Dict. Chem. vol. ii. p. 611.

† Ann. der Chem. und Pharm. vol. lxxiii. p. 86.

salt. The acid when freed from lime and purified, melted at  $202^{\circ}\text{C}$ ., and by analysis gave the following results :—

I.  $\cdot 409$  grm. usnic acid gave  $\cdot 939$  grm. carbonic anhydride and  $\cdot 188$  grm. water.

				I.
$\text{C}_{18}$	=	216	=	62.43
$\text{H}_{18}$	=	18	=	5.20
$\text{O}_7$	=	112	=	32.37
		<hr/>	<hr/>	
		346		100.00

From the above analyses it will be seen that the usnic acid from *Evernia prunastri* is identical in composition with that from *Usnea barbata*. It has the same melting-point, and agrees with it in all its other properties.

#### *Cladonia rangiferina*.

In 1848\* I extracted the lichen acid from *Cladonia rangiferina*, and by analysis found it to have the same composition as usnic acid, with which it agrees very closely in its properties. Hesse, however, observed† that this acid had a different melting-point ( $175^{\circ}\text{C}$ .) from ordinary usnic acid ( $203^{\circ}\text{C}$ .), and proposed, therefore, as it so closely resembled ordinary usnic acid in its general character, to call it  $\beta$ -usnic acid.

#### *Cladonic Acid, $\beta$ -orcin*.

I formerly obtained‡  $\beta$ -orcin by subjecting to destructive distillation a mixture of the acids from *Cladonia rangiferina* and various species of *Usnea*; but I have lately found that ordinary usnic acid, melting at  $203^{\circ}\text{C}$ ., obtained from *Evernia prunastri*, *Ramalina calicaris*, and the various *Usneas*, does not yield a trace of  $\beta$ -orcin when distilled, whilst, on the contrary, the acid extracted from *Cladonia* (Hesse's  $\beta$ -usnic acid melting at  $175^{\circ}\text{C}$ .), on being subjected to the same treatment, yields  $\beta$ -orcin, thus showing a marked difference in the products of its decomposition from ordinary usnic acid, as well as in its melting-point. Under these circumstances, therefore, I think that it would be better to name the acid from *Cladonia rangiferina* "Cladonic Acid," instead of  $\beta$ -usnic acid, as proposed by Hesse.

I expected to have been able to subject cladonic acid to a more careful examination, and procured for that purpose a quantity of *Cladonia rangiferina* from the neighbourhood of Moffat. Unfortunately, however, it was not gathered until the beginning of December, and I was surprised to find that it contained scarcely a trace of cladonic or any similar acid. I intend to obtain a new quantity next summer, when I hope to be more successful.

I cannot conclude this paper without acknowledging the efficient assistance I have received from Mr. Charles E. Groves.

\* Ann. der Chem. und Pharm. vol. lxxiii. p. 98.

† Ibid. vol. cxvii. p. 347.

‡ Ibid. vol. lxxiii. p. 104.